



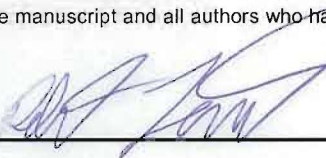
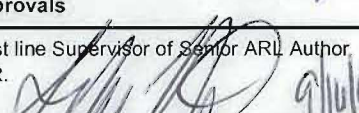
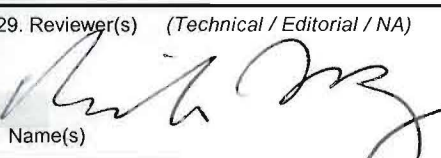


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HIGH-VOLTAGE POLING OF A BULK SAMPLE OF DISPERSE RED 1 POLYMETHYLMETHACRYLATE GUEST-HOST POLYMER FOR U.S. ARMY ELECTRO-OPTICAL APPLICATIONS

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I. INTRODUCTION

Much attention has been paid in recent years to poling thin-film doped polymers for electro-optics applications, mostly in the area of telecommunications switching devices. However, there are applications where a larger thickness of guest-host polymer results in enhanced performance of the electro-optic device, such as in terahertz (THz) generation (Hayden et. al., 2002, Hayden et. al., 2004). The thicker path length available in bulk poled polymers will allow for improved THz power, sensitivity and signal-to-noise ratio in both THz generators and detectors. Large area Pockels cells constructed from electro-optic (EO) guest-host polymers have uses as high speed modulators and shutters, and any application requiring a large d_{33} or r_{33} will potentially benefit from bulk-poled guest-host polymer systems. For large-aperture applications, the optical path length is longer and both poling and operating fields must still be transverse to the direction of light propagation which presents a tremendous challenge in building devices (Figure 1). Given the limitations of thin-film poling for fabricating large-aperture devices, the fabrication of a thick EO polymer slab with the proper orientation is an important goal. Our proposed solution is to pole a thick

slab, cut, polish and re-orient 90 degrees (Figure 2). As a first step towards testing our proposed solution, we describe for the first time the fabrication and poling of a 700 μm thick bulk piece of polymethylmethacrylate (PMMA) doped with various concentrations of Disperse Red 1 (DR1). Maker fringe analysis will demonstrate that under the poling fields currently available to us (57 V/ μm to 71 V/ μm), that substantial ordering of the DR1 chromophores is occurring, resulting in birefringence and significant d_{33} and r_{33} values. In an effort to further improve the EO response of our model bulk DR1 system, we describe the synthesis and thermal characterization of covalently attached DR1 to a tunable high glass transition temperature (T_g) polymeric backbone prepared by ROMP.

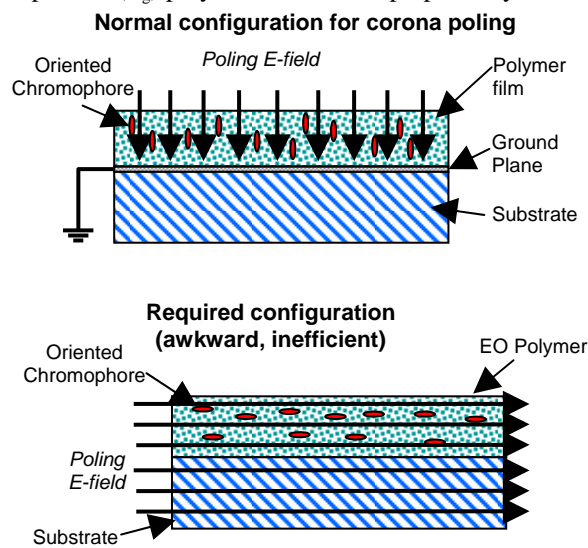


Figure 1. Standard and required poling orientations for E-O materials.

This multi- defense laboratory collaboration is a highly interactive and multi-spectral research effort from molecular modeling, materials development, and system testing. A robust computational effort to predict desired physical properties of EO chromophores such as their EO coefficient and desired wavelength characteristics has been developed. The computational efforts can predict chromophore spectral wavelength characteristics within 30 nm and predict EO performance trends (Andzelm, 2008). This effort allows the chemists to more efficiently synthesize highly active chromophores within desired specifications. Numerous chromophores have been synthesized and have been formulated into polymeric systems via guest-host methodology or direct attachment of the chromophore to the polymer. Via ring opening metathesis polymerization (ROMP), we can attach desired chromophores to a myriad of polymers and control glass

transition temperatures, molecular weight, and other processing properties of the final polymeric materials.

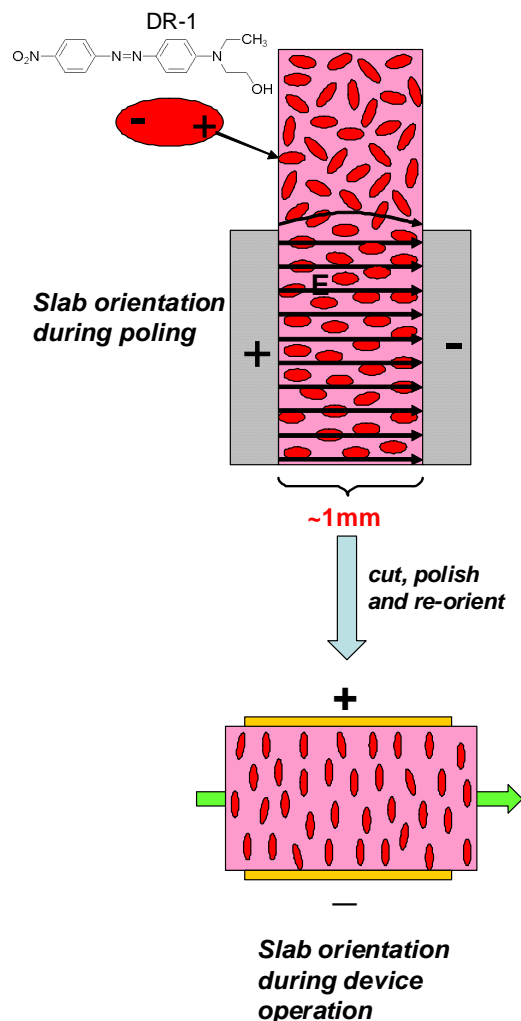


Figure 2. Schematic of proposed solution for fabricating large-aperture devices.

II. EXPERIMENTAL

II-1. Materials

All solvents and reagents were purchased from Aldrich and used as received unless otherwise noted. Compounds **2**, **3**, **4** and 4-(dimethylamino) pyridinium 4-toluene sulfonate (DPTS) were prepared according to the literature. ^1H NMR and ^{13}C NMR data were recorded on a Bruker 600 MHz instrument. All chemical shifts are reported in ppm relative to residual CHCl_3 . Coupling constants (J) are expressed in hertz (Hz). The molecular weight and polydispersity of the polymers was estimated in THF at rt with a Waters 515 HPLC pump. The DR1 chromophore was recrystallized from THF. Polymer guest-host systems were prepared by two different methods; coprecipitation of the DR1 and PMMA from

THF followed by extrusion and by the micro-compounder extrusion method.

The coprecipitation method involves the precipitation of the DR1 chromophore and the PMMA simultaneously from solution. The precipitates are then dried in an oven to remove traces of solvent or moisture that could adversely impact the dielectric breakdown properties of the guest-host polymer. This is followed by compression molding into a thick polymer slab that has smooth surfaces on both sides, allowing for convenient optical measurements.

The micro-compounder method begins with the macroscopic mixing of PMMA and the chosen chromophore. This was accomplished through the use of a vortex mixer or some other high-energy agitation. A DSM Xplore Micro-Compounder was used to perform the physical compounding tasks. A macroscopically mixed polymer blend was charged to the hopper and fed into the extruder. The extruder was fitted with two conical co-rotating screws and also possessed a recycle loop, allowing melt to recirculate through the system automatically. The general processing conditions consisted of the following: the screw rotation rate was 100 rpm, the barrel temperature was 250°C , and the processing cycle was approximately 10 min. A 16 g pre-mixed polymer charge resulted in approximately 13-15 g of polymer. The remainder of the mixed polymer adhered to screw or barrel.

Norbornyl-DR1 monomer (**1**). 5-norbornene-2-carboxylic acid (2.02 g, 15.94 mmol), Disperse Red 1 (5.51g, 17.52 mmol), and DPTS (0.50 g, 1.59 mmol) were dissolved in CH_2Cl_2 (100 mL) and cooled in an ice bath. In a separate flask, DCC (3.94 g, 19.12 mmol) was dissolved in CH_2Cl_2 (25 mL) and transferred via cannula to the above mixture. The reaction mixture was allowed to gradually warm to rt and was allowed to stir overnight (~18 hr). The reaction mixture was vacuum filtered to remove dicyclohexylurea (DCU) and concentrated by rotary evaporation. The crude mixture was dissolved in ethyl acetate (100 mL) and placed in an ice bath for 1 hr to crystallize any remaining DCU. Vacuum filtration, concentration and recrystallization from ethanol produced the title compound (6.1 g, 88 %) as a red solid. endo-norbornyl isomer: ^1H NMR (600 MHz, CDCl_3): δ 1.27-130 (m, 4H), 1.37-1.47 (m, 2H), 1.93 (td, $J = 3.7, 9.4$, 1H), 2.93 (s, 1H), 2.97 (dt, $J = 3.9, 9.4$, 1H), 3.03 (s, 1H), 3.56 (dd, $J = 7.1, 14.3$, 2H), 3.68 (t, $J = 6.3$, 2H), 4.27 (t, $J = 6.3$, 2H), 5.91 (dd, $J = 2.8, 5.6$, 1H), 6.21 (dd, $J = 2.9, 5.6$, 1H), 6.83 (d, $J = 9.1$, 2H), 7.93 (m, 4H), 8.33 (d, $J = 8.8$, 2H) ^{13}C NMR (150 MHz, CDCl_3) δ 12.33, 29.33, 30.47, 41.65, 42.56, 43.11, 43.34, 45.74, 46.42, 46.59, 48.83, 49.72, 61.20, 111.51, 122.67, 124.69, 126.28, 132.20, 135.65, 138.05, 138.17, 143.86, 147.43, 151.33, 156.79, 174.74.

II-2. Representative Polymerization Procedure

A solution of **4** (11.1 mg, 0.013) in CH_2Cl_2 (1 mL) was rapidly injected via syringe into a vigorously stirred solution of **1** (150 mg, 0.34 mmol), **2** (75 mg, 0.49 mmol), and **3** (275 mg, 0.68 mmol) in CH_2Cl_2 (9 mL) at rt. After 30 min, a large excess of ethyl vinyl ether was added to quench the polymerization. The reaction mixture was poured into stirred methanol, and the resulting precipitate was collected by vacuum filtration and dried under high vacuum.

II-3. Sample Preparation.

Figure 3 shows a sample prepared by the coprecipitation or micro-compounder method ready for poling. The polymer sample is approximately 2.5 cm x 2.5 cm x 0.7 mm thick. Two aluminum electrodes fabricated from electron microscopy sample mounts were attached to the polymer sample. The electrodes were polished to allow the electrode intimate contact with the polymer. Methods of attachment included temporary bonding of the aluminum electrode to a 100-200nm vacuum deposited Au pad with Ag paste, and by simple pressure contact of the aluminum stub against the polymer sample with no Au contact pad.

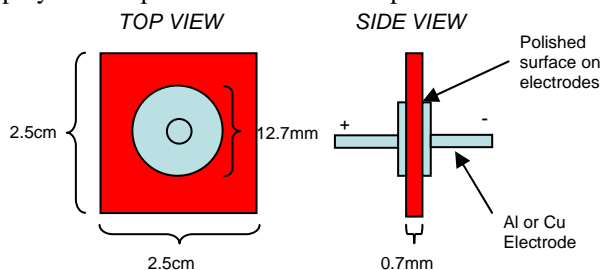


Figure 3. Electrode/sample configuration for poling bulk guest-host polymers.

II-3. Instrumentation and Poling Procedure

A Spellman 100 kV high-voltage DC power supply (Model SL120P60) was used to supply the high voltage required for poling. The sample with attached aluminum electrodes was connected to the power supply and then immersed in silicone oil contained in a Teflon cup. A Teflon cap was placed over the bath to prevent arcing to the walls of the oven. The oven was modified to allow the insulated high voltage lead to enter through the back of the oven. The entire bath/sample assembly was then placed in an oven for poling. To accomplish poling the voltage was increased to 40-50 kV (57 V/ μm to 71 V/ μm) and the temperature ramped to 90°C from ambient (25°C) in approximately 30 min, followed by a period of poling at 90°C for 15 min, then followed by a cool-down with forced nitrogen to 25-35°C over a period of 120-180 min. The high voltage is applied to the sample throughout the entire poling process. When

cooled the voltage is turned off and sample was removed and gently cleaned of the silicone oil with a mild solution of Alconox detergent. The gold pads were removed either by gentle rubbing or by etching with a solution of aqueous potassium iodide. The samples were stored at approximately minus 10°C until measurements were taken.

III. RESULTS AND DISCUSSION

III-1. Bulk Poling of DR1-PMMA Bulk Slab

The as-poled polymers were placed on a rotation stage between crossed polarizers to measure their birefringence. Figure 4 clearly indicates that the DR1-PMMA was poled under the conditions described. The birefringence decayed over a period of several days, an expected property of the DR1-PMMA guest-host system.

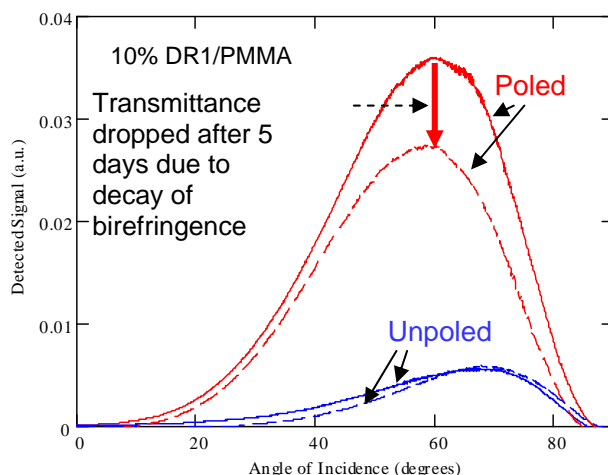


Figure 4. Poling-induced birefringence of 10% DR1-PMMA 700 μm slab.

Further confirmation of poling comes from an examination based on a Maker-fringe fit based on an absorbing isotropic medium (Hayden et al., 1995). The apparatus used in the analysis is shown in Figure 5.

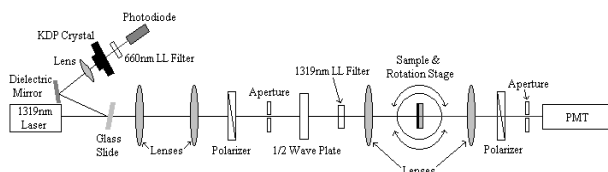


Figure 5. Maker fringe experiment to measure SHG d -coefficient

For observing second-harmonic generation (SHG), the sample was positioned at the waist of a lightly focused (150 mm lens) fundamental beam (1319nm) produced by a diode-pumped Q-switched Nd:YAG laser. The pulse width was 14 ns and the repetition rate 750 Hz. The fundamental beam was polarized inside the laser cavity

and a half-wave plate was used to control the polarization of the beam incident on the sample. For the data shown below, the fundamental beam was p-polarized and a polarizer after the sample was set to for detection of the p-polarized component of the SH output. The SHG signal was detected by a Hamamatsu R928 photomultiplier tube in conjunction with a Stanford Research SR250 boxcar averager. To account for laser power fluctuations, part of the fundamental beam was split off and sent through a lithium iodate crystal to produce a reference second harmonic signal. The sample was mounted on a computer-controlled Oriel rotation stage and data collected by computer at 1-2° increments of the angle of incidence.

Using data from the Maker fringe data at 1319 nm collected on a 10% DR1 coprecipitated sample, the largest d_{33} we were able to measure was an estimated 9 pm/V. In turn we estimate an r_{33} at 1319 nm of 3.7 pm/V. The λ_{max} for the DR1-PMMA system is at 478 nm and therefore we estimate the value of $r_{33} = 6.1$ pm/V at 810 nm. This compares favorably with the highest r_{33} observed in a DR1-copolymer system (7.5 pm/V) (Yardley et. al., 1993). This sample was observed to have an abundance of DR1 precipitates that obscured some of the fine structure in the Maker fringe scan. Subsequent samples (Figure 6) were processed with the micro-compounder extrusion method that yielded samples with a very smooth surface morphology and many fewer particulates. The 10% DR1 (120D, 120Da, 120Db) samples exhibited high-contrast fringes, while the 15% DR1 (124B, 124Ba) samples showed evidence of precipitates while still having a significantly higher SHG response. Further differences can be seen in the type of electrode used for poling. Sample 124B had gold pads whereas sample 124Ba did not. In this case the absence of gold electrodes appears to result in an enhancement, while in the 10% DR1 case it does not. This is likely due to polymer processing variables; one can observe color banding due to the variation in absorption of the DR1 in the PMMA matrix. Optical inhomogeneities due to particulates and concentration gradients accumulating at the leading edge of the extruded polymer as it fills the mold can also be observed.

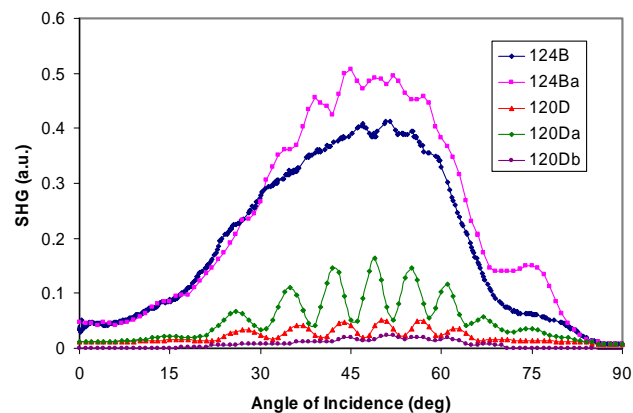


Figure 6. Maker Fringe Fit of X % DR1-PMMA Sample

Comparing the first lot of samples that were made of coprecipitated DR1-PMMA material (~6 pm/V) with the later lots of microcompounded DR1-PMMA material (less than 1 pm/V), it appears that every sample containing particles of DR1 has a higher r_{33} than would normally be expected for such a sample. In addition, there seems to be no clear advantage to using gold pads to assist in the poling process. We expect to circumvent the problem of precipitates by using a copolymer in which the chromophore is chemically bonded to the polymer host. Furthermore, if it is correct that gold pads are not necessary for poling, that will greatly simplify the fabrication of devices.

III-2. Tunable High Glass Transition Electro-Optical Polymers by Ring Opening Metathesis Polymerization

As described above, we are interested in poling bulk EO materials for their potential for enhanced THz generation. One of the challenges in preparing materials for practical applications involves preventing decay of the poling induced polar order for extended periods of time during device operation (Miller et. al., 2000). In our current system, DR1 is doped as a guest in a PMMA matrix. While our initial poling results are promising, the poling induced order quickly decays with time. This is primarily due to the low T_g of the PMMA matrix. The thermal stability can often be improved by tethering the E-O chromophores to high glass-transition (T_g) polymer backbones. Many of the materials prepared in this regard require either demanding reaction conditions unsuitable for the E-O chromophore, post-polymerization modification or are not easily processed (Dalton et. al., 2003). We sought to prepare thermally stable E-O materials via direct polymerization of chromophore containing monomers under mild reaction conditions. Ring opening metathesis polymerization (ROMP) is an attractive alternative to other modes of polymerization because well-defined, high molecular weight polymers can be obtained under undemanding reaction conditions with excellent functional group tolerance (Slugovc, 2004). Thus we anticipate

ROMP will be a viable route to directly produce E-O polymers where the desired chromophore is incompatible with other polymerization methods.

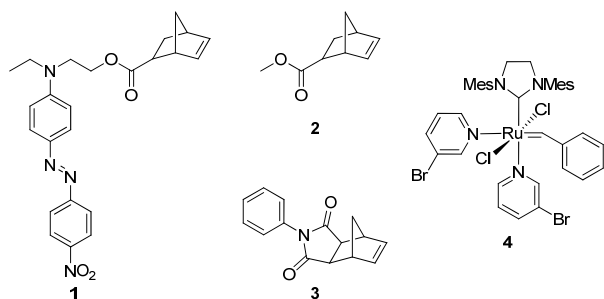


Figure 7. Chemical structures of monomers and catalyst used in this study.

We envisioned copolymerizing an EO chromophore tethered monomer such as **1** with norbornyl-monomers **2** and **3** as a method for preparing polymers with controllable T_g s. Polymers derived from *exo*-*N*-phenylnorbornenedicarboxamide (**2**) are thermally robust with T_g s exceeding 200 °C and soluble in common organic solvents. Modification of the feed ratio between monomers **2** and **3** with constant **1** should enable the preparation of polymers with pre-determined T_g s allowing the material to be tuned according to the desired processing conditions.

We use commercially available Disperse Red 1 (DR1) as a model chromophore for this study which is attached to the polymerizable norbornene unit via DCC/DPTS coupling. Acrylic monomers containing DR1 are difficult to polymerize to high molecular weights by free radical polymerization. It has been previously shown that similar azobenzene-tethered norbornyl-monomers are readily polymerized in a controlled fashion by complex **4** (Moore et. al., 2007).

Monomers **1**, **2**, and **3** were initially homopolymerized in the presence of complex **4** with target molecular weights of 40 kDa. Five copolymer samples were also prepared with target molecular weights of 40 kDa where the weight fraction of monomer **1** in the feedstock was held constant at 30 % while the ratios of monomers **2** and **3** were varied. GPC characterization indicated the polymers were well-defined as evidenced by nearly mono-modal peak shapes and low PDIs (1.1-1.2).

The polymers were characterized by DSC heating from 25 - 200 °C at 10 °C/min with two heating cycles. The values reported were taken from the 2nd heating scan. The T_g s of the homopolymers (Samples P1-P3, Table 1) were used to estimate the values of the copolymers (Samples P4-P8, Table 2) using the Fox equation (Fox, 1956).

Table 1. Thermal Data for E-O Polymers Prepared by ROMP

| Sample | Monomer Feedstock | | | T_g (°C) (calc) | T_g (°C) (DSC) |
|--------|-------------------|------|------|-------------------|------------------|
| | w1 | w2 | w3 | | |
| P1 | 1 | 0 | 0 | - | 103.8 |
| P2 | 0 | 1 | 0 | - | 78.8 |
| P3 | 0 | 0 | 1 | - | 234.8 |
| P4 | 0.3 | 0.7 | 0 | 84.9 | 89.3 |
| P5 | 0.3 | 0.55 | 0.15 | 95.1 | 106.64 |
| P6 | 0.3 | 0.35 | 0.35 | 113.3 | 132.9 |
| P7 | 0.3 | 0.15 | 0.55 | 140.1 | 163.1 |
| P8 | 0.3 | 0 | 0.7 | 170.3 | 189.2 |

^a Calculated according to the Fox equation. ^b Value reported is from 2nd heating cycle.

As anticipated, the T_g of the copolymers increased as the ratio of monomer **2** to **3** was decreased. For a copolymer with 30 wt % of monomer **1**, the T_g can be manipulated from 89 – 189 °C simply by varying to ratios of **2** and **3** in the monomer feedstock. The polymers are also soluble in a variety of common organic solvents and are easily processed under bulk conditions. These characteristics make ROMP a highly attractive method for preparing EO polymers. Preparation of materials that combine high thermal stability and processability were previously difficult to obtain without post-polymerization modification or lattice hardening procedures during poling. The use of ROMP should greatly simplify the overall process and provide materials capable of realizing higher EO coefficients in the bulk.

IV. CONCLUSIONS

In this paper we described the fabrication and poling of a 700µm thick bulk piece of PMMA doped with various concentrations of Disperse Red 1 (DR1). Maker fringe analysis demonstrated that under the poling fields currently available to us (57 V/µm to 71 V/µm), that substantial ordering of the DR1 chromophores is occurring, resulting in birefringence and significant d_{33} and r_{33} values. An estimated value of $r_{33} = 3.7$ pm/V at 1319 nm was measured. The estimated value of r_{33} at 810 nm was 6.1 pm/V. We have shown that this compares favorably with the highest r_{33} observed in a DR1-copolymer system (7.5 pm/V at 800 nm).

There are currently unresolved issues with regard to the role of precipitates in the poling process, as samples with DR1 particulates had more of a response than would be expected of an electro-optic polymer with particulates. We expect to circumvent this by switching to a chromophore-host copolymer in which the chromophore is chemically linked to the host polymer.

Once the difficulties are overcome, poling larger thicknesses of electro-optic polymers will result in

enhanced performance of electro-optic devices in practical applications, such as those currently being investigated for THz generation. The thicker path length available in bulk poled polymers will allow improved THz power, sensitivity and signal-to-noise ratio in both THz generators and detectors. Large area Pockels cells constructed from EO guest-host polymers will find new uses in high speed modulators and shutters, and any application requiring a large d_{33} or r_{33} will potentially benefit from bulk-poled guest-host polymers and copolymers.

As a first step towards chemically linking the chromophore to the host polymer backbone, we explore the use of ROMP for the synthesis of thermally stable E-O polymers. Our initial studies indicate that tunable high T_g EO polymers can be directly prepared in quantitative yields under undemanding reaction conditions. The polymers are soluble in common organic solvents and are readily processed in the bulk. We are in the process of measuring the poling induced of these polymers in both bulk and thin films.

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